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(54) Title: CARBOXYLIC ACID-MODIFIED VINYLIC POLYMERIC COMPOSITIONS

(57) Abstract: This invention relates to novel carboxylic acid-modified vinylic polymeric compositions and the process for preparing them. In particular, the invention relates to novel carboxylic acid-modified vinylic polymeric compositions which exhibit properties that make them useful as support resins for producing polymer latices which can be employed in the formulation of various water-based coatings and inks, particularly flexographic inks. More particularly, these carboxylic acid-modified vinylic polymeric compositions are produced by the addition polymerization reaction of vinylic monomers in the presence of dimer acids, trimer acids, dimerized rosins, or mixtures thereof.



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CARBOXYLIC ACID-MODIFIED VINYLIC POLYMERIC COMPOSITIONS

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FIELD OF INVENTION

This invention relates to novel carboxylic acid-modified vinylic polymeric compositions and the process for preparing them. In particular, the invention relates to novel carboxylic acid-modified vinylic polymeric compositions which exhibit properties that make them useful as support resins for producing polymer latices which can be employed in the formulation of various water-based coatings and inks, particularly flexographic inks. More particularly, these carboxylic acid-modified vinylic polymeric compositions are produced by the addition polymerization reaction of vinylic monomers in the presence of dimer acids, trimer acids, dimerized rosins, or mixtures thereof.

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BACKGROUND OF THE INVENTION

It is highly desirable that ink and overprint formulations utilized for graphic art applications possess certain high performance characteristics. As typical surfactant-based emulsion polymerization products do not have the desired rheology properties for such applications, it is common practice to add a support resin in place of, or in addition to, the surfactants. These water and alkaline soluble (at pHs of about 8) support resins are added to the emulsion polymerization reaction to improve the stability and rheological properties of the latex. Improved stability results from absorption of the support resin on the surface of the particles and the increased viscosity of the emulsion.

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The traditional processes for producing polymeric support resins are well-known (see generally U.S. Patent Nos. 4,839,413 and 5,216,064, which are hereby incorporated by reference). Commonly a solution polymerization reaction is employed wherein styrenic monomer and acrylic acid is mixed with a hydrocarbon solvent, a polymerization initiator, and a chain transfer agent. Upon completion of the reaction, the solution is stripped of the solvent to yield the acrylic polymer. The polymer is then available for use as a support resin when dissolved in an ammoniacal water solution.

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However, problems exist with these traditional methods of producing support resins. For example, these methods require the use of environmentally adverse hydrocarbon solvents. Moreover, as these solvents are not usable or desirable in water-based ink or overprint formulations, the solvents must be stripped from the resulting acrylic polymers (thereby causing a yield loss). This stripping step also adds expense to the process due to both the loss of yield and the energy consumed in performing the stripping.

U. S. Patent No. 6,172,149, which is incorporated herein by reference, teaches the preparation of rosin-fatty acid vinyl polymer sizing compositions via a polymerization method which does not require the use of hydrocarbon solvents. However, a problem exists with the employment of such polymers as support resins for emulsion polymerizations in that the resultant polymer emulsions are relatively low in viscosity when compared to similar latices made with acrylic support resins produced by conventional techniques. These low viscosities render the latices unsuitable for certain applications, such as architectural paints and flexographic inks. Another shortcoming is that the use of support resins based on unsaturated fatty acids yields latices with relatively high levels of residual monomers. These high levels of residuals can cause a latex to have a strong odor that most potential users of the latex find objectionable. A further disadvantage inherent in the use of both conventional acrylic support resins and the polymers taught in U. S. Patents No. 6,172,149 lies in the fact that inks and coatings based on latices made with these resins commonly exhibit relatively low resistances to commercial cleaning formulations containing glycol ethers (such as FORMULA 409 available from the Clorox Co.) or alkaline chemicals. Resistance to these types of commercial cleaning formulations is highly desired, especially in inks employed in the printing of consumer packaging materials.

Therefore, an object of this invention is to solve these major problems by disclosing a method of producing carboxylic acid-modified vinyl polymeric compositions.

Another object of this invention is to disclose carboxylic acid-modified vinyl polymeric compositions which exhibit properties that make them useful as support resins in water-based graphic art ink and coating applications.

SUMMARY OF THE INVENTION

The objects of this invention are met via a method that employs dimer acids, trimer acids, functional equivalents of dimer acid, functional equivalents of trimer acid, and/or dimerized rosins to act as solvents in the polymerization reaction of acrylic and/or styrenic monomers, thereby producing carboxylic acid-modified vinylic polymer compositions which are useful as support resins in water-based graphic art ink and coating applications. As this method does not require the use of hydrocarbon solvents, the need for solvent stripping is eliminated. Also, when employed as support resins in emulsion polymerizations the resultant emulsions have relatively high viscosity, relatively low levels of residual monomers, and improved resistance to alkaline chemicals and glycol ethers.

DESCRIPTION OF THE PREFERRED EMBODIMENT

- The method for producing carboxylic acid-modified vinylic polymeric compositions comprises reacting in a free-radical addition polymerization reaction:
- (A) about 40.0% to about 80.0% by total weight of the reactants of a monomer mixture comprising:
 - (1) about 15.0% to about 45.0% by total weight of the monomer mixture of a member selected from the group consisting of acrylic acid, methacrylic acid, fumaric acid, maleic anhydride, itaconic acid, and combinations thereof,
 - (2) about 55.0% to about 85.0% by total weight of the monomer mixture of a member selected from the group consisting of non-carboxylic acid-containing vinylic monomers and combinations thereof,
 - (3) a catalytic amount of polymerization initiator, and
 - (4) up to about 4.0% by total weight of the monomer mixture of chain transfer agent; and
 - (B) about 20.0% to about 60.0% by total weight of the reactants of a carboxylic acid mixture comprising:
 - (1) about 20.0% to about 100.0% by total weight of the carboxylic acid mixture of a member selected from the group consisting of dimer

acids, trimer acids, functional equivalents of dimer acid, functional equivalents of trimer acid, dimerized rosins, and combinations thereof,

(2) up to about 80.0% by total weight of the carboxylic acid mixture of a member selected from the group consisting of rosins, unsaturated fatty acids, and combinations thereof, and

(3) up to about 0.1% by total weight of the carboxylic acid mixture of bleaching agent;

at a temperature in the range of about 135°C to about 220°C to produce a carboxylic acid-modified vinylic polymeric composition having a weight average molecular weight in the range of about 4,000 to about 20,000 and an acid number in the range of about 160 to about 260.

A preferred method for producing carboxylic acid-modified vinylic polymeric compositions comprises reacting in a free-radical addition polymerization reaction:

(A) about 40.0% to about 80.0% by total weight of the reactants of a monomer mixture comprising:

(1) about 20.0% to about 35.0% by total weight of the monomer mixture of a member selected from the group consisting of acrylic acid, methacrylic acid, fumaric acid, maleic anhydride, itaconic acid, and combinations thereof,

(2) about 65.0% to about 80.0% by total weight of the monomer mixture of a member selected from the group consisting of non-carboxylic acid-containing vinylic monomers and combinations thereof,

(3) a catalytic amount of polymerization initiator, and

(4) about 0.5% to about 2.0% by total weight of the monomer mixture of chain transfer agent; and

(B) about 20.0% to about 60.0% by total weight of the reactants of a carboxylic acid mixture comprising:

(1) about 50.0% to about 100.0% by total weight of the carboxylic acid mixture of a member selected from the group consisting of dimer acids, trimer acids, functional equivalents of dimer acid, functional equivalents of trimer acid, dimerized rosin, and combinations thereof,

(2) up to about 50.0% by total weight of the carboxylic acid mixture of a member selected from the group consisting of rosins, unsaturated fatty acids, and combinations thereof, and

(3) up to about 0.1% by total weight of the carboxylic acid mixture of bleaching agent;

at a temperature in the range of about 145°C to about 210°C to produce a carboxylic acid-modified vinylic polymeric composition having a weight average molecular weight in the range of about 4,000 to about 20,000 and an acid number in the range of about 180 to about 250.

The carboxylic acid components function as solvents in the polymerization reaction of the acrylic monomers. Additionally, while a portion of the carboxylic acids remain unreacted, some of the carboxylic acids may become graft polymerized onto the acrylic. The resulting carboxylic acid-modified vinylic polymer compositions have a weight average molecular weight in the range of about 4,000 to about 20,000; with the preferred molecular weights being in the range of about 5,000 to about 11,000.

Carboxylic acid-modified vinylic polymer compositions produced via the present method have an acid number in the range of about 160 to about 260. It is preferred that the carboxylic acid-modified vinylic polymer compositions have an acid number in the range of about 180 to about 250.

The free-radical addition polymerization reaction used to produce the carboxylic acid-modified vinylic polymeric composition is a melt polymerization reaction in which no water is employed. Reaction temperatures suitable for use in the present method are within the range of about 135°C to about 220°C; with the preferred temperatures being in the range of about 145°C to about 210°C.

From about 15.0% to about 45.0% (preferably from about 20.0% to about 35.0%) by total weight of the monomer mixture employed in the free-radical addition polymerization reaction is a member selected from the group consisting of acrylic acid, methacrylic acid, fumaric acid, maleic anhydride, itaconic acid, and combinations thereof.

From about 55.0% to about 85.0% (preferably from about 65.0% to about 80.0%) by total weight of the monomer mixture is non-carboxylic acid-containing vinylic monomers. Preferred non-carboxylic acid-containing vinylic monomers

include, but are not limited to the following: styrene, substituted styrenes, acrylic esters, methacrylic esters, acrylamides, methacrylamides, acrylonitrile, methacrylonitrile, vinyl esters, vinyl chloride, vinylidene chloride, vinylpyridines, N-vinylamides, vinyl ethers, and combinations thereof.

- 5 Preferred substituted styrenes suitable for use in the present invention include, but are not limited to, the following: \forall -methylstyrene, m-methylstyrene, p-methylstyrene, p-tert-butylstyrene, chlorostyrenes, 3-chloromethylstyrene, 4-chloromethylstyrene, and combinations thereof.

- Preferred acrylic esters suitable for use in the present invention include, but are not limited to, the following: methyl acrylate, ethyl acrylate, butyl acrylate, isobutyl
10 acrylate, cyclohexyl acrylate, 2-ethylhexyl acrylate, isodecyl acrylate, lauryl acrylate, stearyl acrylate, isobornyl acrylate, benzyl acrylate, hydroxyethyl acrylate, hydroxypropyl acrylate, hydroxybutyl acrylate, methoxyethyl acrylate, ethoxyethyl acrylate, phenoxyethyl acrylate, tetrahydrofurfuryl acrylate, glycidyl acrylate,
15 dimethylaminoethyl acrylate, diethylaminoethyl acrylate, and combinations thereof.

- Preferred methacrylic esters suitable for use in the present invention include, but are not limited to, the following: methyl methacrylate, ethyl methacrylate, butyl methacrylate, isobutyl methacrylate, cyclohexyl methacrylate, 2-ethylhexyl methacrylate, isodecyl methacrylate, lauryl methacrylate, stearyl methacrylate, isobornyl
20 methacrylate, benzyl methacrylate, hydroxyethyl methacrylate, hydroxypropyl methacrylate, methoxyethyl methacrylate, ethoxyethyl methacrylate, phenoxyethyl methacrylate, tetrahydrofurfuryl methacrylate, glycidyl methacrylate, dimethylaminoethyl methacrylate, diethylaminoethyl methacrylate, tert-butylaminoethyl methacrylate, acetoxyethyl methacrylate, and combinations thereof.

- 25 Preferred acrylamides suitable for use in the present invention include, but are not limited to, the following: acrylamide, N-methylolacrylamide, N-butoxyethylacrylamide, N,N-dimethylacrylamide, N-isopropylacrylamide, N-tert-butylacrylamide, N-tert-octylacrylamide, diacetone acrylamide, and combinations thereof.

- 30 Preferred methacrylamides suitable for use in the present invention include, but are not limited to, the following: methacrylamide, N-methylolacrylamide, N,N-dimethylacrylamide, and combinations thereof.

Preferred vinyl esters suitable for use in the present invention include, but are not limited to, the following: vinyl acetate, vinyl propionate, vinyl 2-ethylhexanoate, vinyl neodecanoate, vinyl stearate, and combinations thereof.

Preferred N-vinylamides suitable for use in the present invention include, but are not limited to, the following: N-vinylpyrrolidione, N-vinylcaprolactam, N-vinylformamide, N-vinylacetamide, and combinations thereof.

Preferred vinyl ethers suitable for use in the present invention include, but are not limited to, the following: methyl vinyl ether, ethyl vinyl ether, butyl vinyl ether, decyl vinyl ether, hydroxybutyl vinyl ether, and combinations thereof.

A catalytic amount of polymerization initiator is used in the free radical polymerization reaction. The amount of initiator employed commonly comprises from about 0.5% to about 5.0% (preferably from about 0.2% to about 2.0%) by total weight of the monomer mixture. Traditional free radical polymerization initiators (such as thermal initiators, redox initiators, and the like) are suitable for use in the polymerization reaction. The type of initiator suitable for use in the present invention is known in the art to depend upon the desired temperature for the reaction. Examples of suitable thermal initiators include, but are not limited to, the following: hydrogen peroxide, t-butyl hydroperoxide, di-t-butyl peroxide, benzoyl peroxide, benzoyl hydroperoxide, 2,4-dichlorobenzoyl peroxide, t-butyl peracetate, azobisisobutyronitrile, isopropyl peroxy carbonate, 2,2'-azobis[2-methyl-N-(2-hydroxyethyl)propionamide], 2,2'-azobis(N-butyl-2-methylpropionamide), 2,2'-azobis(N-cyclohexyl-2-methylpropionamide), and combinations thereof. Examples of suitable redox initiators include, but are not limited to, the following: cumene hydroperoxide-sodium metabisulfite, cumene hydroperoxide-iron (II) sulfate, and combinations thereof.

Where desired, a chain transfer agent may be employed in the present method. Chain transfer agents which are suitable for use in the above reaction include, but are not limited to, the following: dodecyl mercaptan, mercaptoacetic acid, mercaptopropionic acid, mercaptosuccinic acid, octyl mercaptan, 2-mercaptoethanol, and combinations thereof. Where employed, it is preferred to use an amount of chain transfer agent in the range of from about 0.5% to about 2.0% by total weight of the monomer mixture of chain transfer agent.

From about 20.0% to about 100.0% (preferably from about 50.0% to about 100.0%) by total weight of the carboxylic acid mixture is a member selected from the group consisting of dimer acids, trimer acids, functional equivalents of dimer acid, functional equivalents of trimer acid, dimerized rosin, and combinations thereof.

5 Dimer acids suitable for use in the present invention are made by dimerizing unsaturated fatty acids to produce a mixture of dicarboxylic acids containing approximately 32 to 48 carbon atoms. Likewise, suitable trimer acids are made by trimerizing unsaturated fatty acids to produce a mixture of tricarboxylic acids containing approximately 48 to 72 carbon atoms. Typical suitable dimer acids and
10 trimer acids are supplied commercially by Cognis Corporation under the trade name EMPOL and by Uniqema Corporation under the trade name PRIPOL.

For the purposes of this invention, a functional equivalent of dimer acid contains two carboxyl groups and from 19 to 27 carbon atoms. An example of a functional equivalent of dimer acid is the 21-carbon dicarboxylic acid produced by
15 Diels-Alder adduction of an unsaturated fatty acid with acrylic acid. A typical such Diels-Alder adduct is supplied commercially by MeadWestvaco Corporation as DIACID 1550. Another example of a functional equivalent of dimer acid suitable for use in the present invention is the 19-carbon dicarboxylic acid produced by the oxo reaction of oleic acid followed by oxidation of the resulting aldehyde.

20 For the purposes of this invention, a functional equivalent of trimer acid contains three carboxyl groups and from 20 to 28 carbon atoms. An example of a functional equivalent of trimer acid is produced by the oxo reaction of linoleic acid.

A detailed discussion of the manufacture and properties of dimer acids, trimer acids, and their functional equivalents can be found in the Kirk-Othmer Encyclopedia
25 of Chemical Technology, 4th Edition, volume 8, pp. 223-237, which is incorporated herein by reference.

Examples of dimerized rosins which are suitable for use in the present invention includes rosins that have been partially or fully dimerized by means of heat and an acidic catalyst. Typical commercially available dimerized rosins are DIMEREX
30 (available from the Hercules Corp.) and RESIN P (available from Resinas Sintéticas). The chemistry and synthesis of dimerized rosins is discussed in detail in *Progress in*

Organic Coatings, vol. 20, pp 139-167 (1992) and references therein, which are incorporated herein by reference.

Where desired, up to about 80.0% (preferably up to about 50.0%) by total weight of the carboxylic acid mixture can be a member selected from the group
5 consisting of rosins, unsaturated fatty acids, and combinations thereof. Rosins suitable for optional use in the present invention include gum rosin, tall oil rosin, wood rosin, and combinations thereof.

Unsaturated fatty acids suitable for optional use in the present invention are fatty acids containing about 12 to about 24 carbon atoms and at least one carbon-carbon
10 double bond. Preferred fatty acids include, but are not limited to, the following: oleic acid, linoleic acid, linolenic acid, eleostearic acid, tall oil fatty acids, linseed oil fatty acids, tung oil fatty acids, safflower oil fatty acids, soybean oil fatty acids, and combinations thereof.

A small amount of a bleaching agent can be added to prevent the formation of
15 color bodies during the polymerization reaction, but it is not essential to the practice of the invention. Any compatible bleaching agent (such as hypophosphorous acid and the like) or combination of bleaching agents can be utilized.

The preferred method of carrying out the free-radical addition polymerization reaction of the current invention is to charge a reaction vessel with the dimer acid,
20 trimer acid, functional equivalent of dimer acid, functional equivalent of trimer acid, dimerized rosin, or combinations thereof together with the optional rosin and/or unsaturated fatty acid and then heat the contents of the reaction vessel with stirring to a temperature in the range of about 135°C to about 220°C (preferably about 145°C to about 210°C). The vinylic monomers, initiator, and optional chain transfer agent are
25 then added to the reaction vessel continuously over a period of about one to about five hours (preferably about two to about four hours). After the monomer addition is complete, the reaction is continued at the specified temperature for up to an additional five hours (preferably an additional one to three hours) to complete the addition polymerization reaction.

30 The resulting polymeric compositions can be used as support resins for the free-radical emulsion polymerization of vinylic monomers by methods that are well known in the art to produce latices that are useful as binders for inks (particularly flexographic

inks) and other coatings. The latices thus produced show higher viscosities, lower residual monomer levels, and increased resistance to alkaline chemicals and glycol ethers in their dried state when compared with comparable latices made with support resins that do not contain dimer acid, trimer acid, or dimerized rosin.

5 Water-based inks and other coatings can be formulated by employing a latex comprising as a support resin an aqueous solution of the instant carboxylic acid-modified vinylic polymeric compositions with desired pigment. As used herein the term "pigment" refers to a water-insoluble colorant. Any pigment that is compatible with water-based inks may be employed in the practice of the invention. It is well
10 within the ability of one skilled in the art to employ the carboxylic acid-modified vinylic polymeric compositions taught herein to produce such latexes, inks, and coatings.

 The carboxylic acid-modified vinylic polymeric compositions may also be employed to formulate aqueous varnishes for use on substrates such as wood, concrete,
15 brick, masonry, and the like. Where desired, pigment can be added to the varnish in order to formulate aqueous paints for use on these substrates. Any pigment that is compatible with aqueous paints may be employed in the practice of the invention. It is well within the ability of one skilled in the art to employ the carboxylic acid-modified vinylic polymeric compositions taught herein to produce such sealants and paints.

20 The following examples are provided to further illustrate the present invention and are not to be construed as limiting the invention in any manner.

EXAMPLE 1

 A carboxylic acid-modified vinylic polymeric composition was prepared as
25 follows. To a 500-ml round bottom flask equipped with a stirrer, heating mantle, reflux condenser, and addition funnel was charged 109.1 g of EMPOL 1018 (a dimer acid available from Cognis Corp.) and 0.07 g of hypophosphorous acid. The charge was heated with stirring to 175°C, and the addition of a monomer mixture consisting of 74.9 g of styrene, 74.9 g of α -methylstyrene, 92.4 g of acrylic acid, and 3.76 g of di-tert-
30 butyl peroxide was started. The monomer mixture was added over two hours, during which time the temperature of the batch was increased to 180°C. After the monomer addition was complete, stirring was continued for an additional hour at 180°C. Then an

additional 0.39 g of di-tert-butyl peroxide was charged, and stirring was continued for an additional two hours to complete the polymerization reaction. The carboxylic acid-modified vinylic polymeric composition obtained upon cooling of the reaction mass (hereinafter referred to as "Polymer No. 1") had a ring-and-ball softening point of
5 130°C, an acid number of 230, and a weight average molecular weight of 5550.

EXAMPLE 2

A carboxylic acid-modified vinylic polymeric composition was prepared as follows. To a 500-ml round bottom flask equipped with a stirrer, heating mantle, reflux condenser, and addition funnel was charged 71.6 g of EMPOL 1045 (a trimer acid
10 available from Cognis Corp.), 37.5 g of SS rosin (a tall oil rosin available from MeadWestvaco Corp.), and 0.07 g of hypophosphorous acid. The charge was heated with stirring to 175°C, and the addition of a monomer mixture consisting of 74.9 g of styrene, 74.9 g of α -methylstyrene, 92.4 g of acrylic acid, and 3.76 g of di-tert-butyl peroxide was started. The monomer mixture was added over two hours at 175°C.
15 After the monomer addition was complete, stirring was continued for an additional hour during which time the temperature was increased to 210°C. Then an additional 0.39 g of di-tert-butyl peroxide was charged, and stirring was continued for an additional two hours to complete the polymerization reaction. The carboxylic acid-modified vinylic polymeric composition obtained upon cooling of the reaction mass (hereinafter referred
20 to as "Polymer No. 2") had a ring-and-ball softening point of 144°C, an acid number of 224, and a weight average molecular weight of 5420.

EXAMPLE 3

A carboxylic acid-modified vinylic polymeric composition was prepared as follows. To a 500-ml round bottom flask equipped with a stirrer, heating mantle, reflux condenser, and addition funnel was charged 71.6 g of DIACID 1550 (a C-21 dicarboxylic acid available from MeadWestvaco Corp.), 37.5 g of SS rosin (a tall oil rosin available from MeadWestvaco Corp.) and 0.07 g of hypophosphorous acid. The charge was heated with stirring to 175°C, and the addition of a monomer mixture consisting of 74.9 g of styrene, 74.9 g of α -methylstyrene, 92.4 g of acrylic acid, and 3.76 g of di-tert-butyl peroxide was started. The monomer mixture was added over two hours, during which time the temperature of the batch was increased to 185°C. After the monomer addition was complete, stirring was continued for an additional hour at 185°C. Then an additional 0.39 g of di-tert-butyl peroxide was charged, and stirring was continued for an additional two hours at 190°C to complete the polymerization reaction. The carboxylic acid-modified vinylic polymeric composition obtained upon cooling of the reaction mass (hereinafter referred to as "Polymer No. 3") had a ring-and-ball softening point of 134°C, an acid number of 246, and a weight average molecular weight of 4500.

EXAMPLE 4

A carboxylic acid-modified vinylic polymeric composition was prepared as follows. To a 500-ml round bottom flask equipped with a stirrer, heating mantle, reflux condenser, and addition funnel was charged 71.6 g of oleic acid, 37.5 g of DIMEREX (a dimerized rosin available from Hercules Inc.), and 0.07 g of hypophosphorous acid. The charge was heated with stirring to 175°C, and the addition of a monomer mixture consisting of 74.9 g of styrene, 74.9 g of α -methylstyrene, 92.4 g of acrylic acid, and 3.76 g of di-tert-butyl peroxide was started. The monomer mixture was added over two hours, during which time the temperature was gradually increased to 190°C. After the monomer addition was complete, stirring was continued for an additional hour, during which time the temperature was gradually increased to 200°C. Then an additional 0.39 g of di-tert-butyl peroxide was charged, and stirring was continued for an additional two hours at 200°C to complete the polymerization reaction. The carboxylic acid-modified vinylic polymeric composition obtained upon cooling of the reaction mass (hereinafter

referred to as "Polymer No. 4") had a ring-and-ball softening point of 125°C and an acid number of 251.

EXAMPLE 5

For comparison purposes, a rosin-fatty acid vinylic polymer was prepared as follows. To a 500-ml round bottom flask equipped with a stirrer, heating mantle, reflux condenser, and addition funnel was charged 71.6 g of L-5 fatty acid (a tall oil fatty acid available from MeadWestvaco Corp.), 37.5 g of SS rosin (a tall oil rosin available from MeadWestvaco Corp.), and 0.07 g of hypophosphorous acid. The charge was heated with stirring to 175°C, and the addition of a monomer mixture consisting of 74.9 g of styrene, 74.9 g of γ -methylstyrene, 92.4 g of acrylic acid, and 3.76 g of di-tert-butyl peroxide was started. The monomer mixture was added over two hours at 173°C. After the monomer addition was complete, stirring was continued for an additional hour at 175°C. Then an additional 0.39 g of di-tert-butyl peroxide was charged, and stirring was continued for an additional two hours at 175°C to complete the polymerization reaction. The rosin-fatty acid vinylic polymer obtained upon cooling of the reaction mass (hereinafter referred to as the "Comparison Polymer") had a ring-and-ball softening point of 125°C, an acid number of 235, and a weight average molecular weight of 4780.

A latex was produced as follows using the Comparison Polymer as a support resin. To a 200 ml round-bottomed flask fitted with a stirrer, heating mantle, thermometer, and monomer addition pump was charged 409.1 g of deionized water, 104.8 g of the Comparison Polymer, and 20.0 g of 28% aqueous ammonia. The batch was heated with stirring to 70°C to dissolve the resin. The batch was then heated to 82°C, and a solution of 1.16 g of ammonium persulfate and 0.18 g of 28% aqueous ammonia in 13.6 g of deionized water was charged. Stirring was continued at 82°C while a monomer feed comprising 99.3 g of styrene, 167.1 g of methyl methacrylate, and 108.3 g of 2-ethylhexyl acrylate and an initiator feed comprising 1.16 g of ammonium persulfate, 0.26 g of 28% aqueous ammonia, and 65.9 g of deionized water were added concurrently over two hours. The batch was then held for thirty minutes at 82°C, a solution of 1.16 g of ammonium persulfate and 0.18 g of 28% aqueous ammonia in 13.6 g of deionized water was charged, and the batch was then held at 82°C for an additional hour to complete the reaction. The resulting latex had a solids content

of 48.1%, a viscosity of 94 cP, and a level of residual 2-ethylhexyl acrylate of 2795 ppm.

EXAMPLE 6

A latex was produced following the procedure of Example 5, wherein the
5 Comparison Polymer was replaced with Polymer No. 1. The resultant latex had a solids content of 47.6% and a viscosity of 1170 cP (which is a significant increase in viscosity over the latex made with the Comparison Polymer). Furthermore, the level of residual 2-ethylhexyl acrylate in this latex was 987 ppm, which substantially below the residual level contained in the Comparison Polymer's latex.

EXAMPLE 7

10 A latex was produced following the procedure of Example 5, wherein the Comparison Polymer was replaced with Polymer No. 2. The resultant latex was tested for resistance to FORMULA 409 (a commercial cleaner available from the Clorox Co.) in the following manner. A sample of the latex was drawn down on a Leneta card with
15 a 3-mil Byrd applicator. The drawdown was allowed to dry for three days at room temperature. Then a drop of FORMULA 409 cleaner was placed on the dried latex film and allowed to stand for 15 minutes. The FORMULA 409 drop was then wiped off, and the degree of etching of the polymer film was rated on a scale of 1-5 (with 1 being essentially complete disruption of the film and 5 being no noticeable effect). The latex
20 made with Polymer No. 2 rated 3 versus a rating of 2 for the latex made with the Comparison Polymer.

EXAMPLE 8

A latex was produced following the procedure of Example 5, wherein the
Comparison Polymer was replaced with Polymer No. 3. The level of residual 2-
25 ethylhexyl acrylate in this latex was 487 ppm (significantly below the level of 2795 ppm in the latex made with the Comparison Polymer). Likewise, the present latex exhibited a superior FORMULA 409 resistance rating of 3.5.

EXAMPLE 9

A latex was produced following the procedure of Example 5, wherein the
30 Comparison Polymer was replaced with Polymer No. 4. The resulting latex exhibited a superior FORMULA 409 resistance rating of 4.

EXAMPLE 10

A water-based flexographic ink can be made from the latex of Example 9 by stirring together 34 parts by weight of FLEXIVERSE BFD1121 (a phthalocyanine blue pigment dispersion available from Sun Chemical Corp.), 60 parts of the latex of Example 9, 5 parts of PE-392N35 (a polyethylene wax dispersion available from Chemcor Chemical Corp.), and 1 part of DOW 51 (a defoamer available from Dow Chemical Co.).

EXAMPLE 11

A water-based, high-gloss overprint varnish can be made from the latex of Example 8 by stirring together 89 parts by weight of the latex of Example 8, 5 parts of water, 0.1 part of FOAMBLAST 340 (a defoamer available from ROSS Chem Inc.), 3.5 parts of PEW-392N35 (a polyethylene wax dispersion available from Chemcor Chemical Corp.), and 2.4 parts of SURFYNOL 420 (a surfactant available from Air Products and Chemicals Inc.).

EXAMPLE 12

A white architectural paint can be made from the latex of Example 6 as follows. A pigment concentrate is made by grinding 200 parts by weight of titanium dioxide pigment in a mixture of 100 parts of water, 2 parts of NATROSOL Plus 330 (a rheology modifier available from Hercules, Inc.), 11.1 parts of TAMOL 165A (a dispersant available from Rohm & Haas Co.), 2.2 parts of IGEPAL CTA 639W (a dispersant available from Rhodia), 1.9 parts of 28% aqueous ammonia, and 1 part of BYK 022 (a defoamer available from ByK-Chemie USA). This pigment concentrate is then let down with 29.7 parts of water, 1.9 parts of RHODOLINE 645 (a defoamer available from Rhodia), 587.2 parts of the latex of Example 6, 5.8 parts of SURFYNOL 104DPM (a surfactant available from Air Products and Chemicals Inc.), 9.3 parts of SANTICIZER 160 (a plasticizer available from Solutia Inc.), 23.6 parts of VELATE 368 (a plasticizer available from Velsicol Chemical Corp.), 8.1 parts of NUOCURE CK-10 (a drier available from CONDEA Servo LLC), 1.9 parts of 28% aqueous ammonia, and a solution of 6 parts of POLYPHOBE 115 (a rheology modifier available from Union Carbide Corp.) in 16.7 parts of water.

Many modifications and variations of the present invention will be apparent to one of ordinary skill in the art in light of the above teachings. It is therefore understood

that the scope of the invention is not to be limited by the foregoing description, but rather is to be defined by the claims appended hereto.

What is claimed is:

1. A method for producing carboxylic acid-modified vinylic polymeric compositions which comprises reacting in a free-radical addition polymerization reaction:
 - (A) About 40% to about 80% by total weight of the reactants of a monomer mixture comprising:
 - (1) about 15.0% to about 45.0% by total weight of the mixture of a member selected from the group consisting of acrylic acid, methacrylic acid, fumaric acid, maleic anhydride, itaconic acid, and combinations thereof,
 - (2) about 55.0% to about 85.0% by total weight of the mixture of a member selected from the group consisting of non-carboxylic acid-containing vinylic monomers and combinations thereof,
 - (3) a catalytic amount of polymerization initiator, and
 - (4) up to about 4.0% by total weight of the mixture of chain transfer agent, and
 - (B) about 20% to about 60% by total weight of the reactants of a carboxylic acid mixture comprising:
 - (1) about 20.0% to about 100.0% by total weight of the mixture of a member selected from the group consisting of dimer acids, trimer acids, functional equivalents of dimer acid, functional equivalents of trimer acid, dimerized rosins, and combinations thereof;
 - (2) up to about 80.0% by total weight of the mixture of a member selected from the group consisting of rosins, unsaturated fatty acids, and combinations thereof; and
 - (3) up to about 0.1% by total weight of the mixture of bleaching agent,
- at a temperature in the range of about 135°C to about 220°C to produce a carboxylic acid-modified vinylic polymeric composition having a weight average molecular weight in the range of about 4,000 to about 20,000 and an acid number in the range of about 160 to about 260.

2. The method of claim 1 which comprises reacting in a free-radical addition polymerization reaction:

(A) About 40% to about 80% by total weight of the reactants of a monomer mixture comprising:

- 5 (1) about 20.0% to about 35.0% by total weight of the mixture of a member selected from the group consisting of acrylic acid, methacrylic acid, fumaric acid, maleic anhydride, itaconic acid, and combinations thereof,
- 10 (2) about 65.0% to about 80.0% by total weight of the mixture of a member selected from the group consisting of non-carboxylic acid-containing vinylic monomers and combinations thereof,
- (3) a catalytic amount of polymerization initiator, and
- (4) about 0.5% to about 2.0% by total weight of the mixture of chain transfer agent, and

15 (B) about 20% to about 60% by total weight of the reactants of a carboxylic acid mixture comprising:

- (1) about 50.0% to about 100.0% by total weight of the mixture of a member selected from the group consisting of dimer acids, trimer acids, functional equivalents of dimer acid, functional equivalents of trimer acid, dimerized rosins, and combinations thereof;
- 20 (2) up to about 50.0% by total weight of the mixture of a member selected from the group consisting of rosins, unsaturated fatty acids, and combinations thereof; and
- (3) up to about 0.1% by total weight of the mixture of bleaching agent,

25 at a temperature in the range of about 145°C to about 210°C to produce a carboxylic acid-modified vinylic polymeric composition having a weight average molecular weight in the range of about 4,000 to about 20,000 and an acid number in the range of about 160 to about 260.

3. The method of claim 1 wherein the carboxylic acid-modified vinylic polymer composition has a weight average molecular weight in the range of about 5,000 to about 11,000.

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4. The method of claim 1 wherein the carboxylic acid-modified vinylic polymer composition has an acid number in the range of about 180 to about 250.

5. The method of claim 1 wherein the non-carboxylic acid-containing vinylic monomer is a member selected from the group consisting of styrene, substituted
5 styrenes, acrylic esters, methacrylic esters, acrylamides, methacrylamides, acrylonitrile, methacrylonitrile, vinyl esters, vinyl chloride, vinylidene chloride, vinylpyridines, N-vinylamides, vinyl ethers, and combinations thereof.

6. The method of claim 5 wherein the non-carboxylic acid-containing vinylic monomer is a member selected from the group consisting of \forall -methylstyrene, m-
10 methylstyrene,
p-methylstyrene, p-tert-butylstyrene, chlorostyrenes, 3-chloromethylstyrene, 4-chloromethylstyrene, methyl acrylate, ethyl acrylate, butyl acrylate, isobutyl acrylate, cyclohexyl acrylate, 2-ethylhexyl acrylate, isodecyl acrylate, lauryl acrylate, stearyl acrylate, isobornyl acrylate, benzyl acrylate, hydroxyethyl acrylate, hydroxypropyl
15 acrylate, hydroxybutyl acrylate, methoxyethyl acrylate, ethoxyethyl acrylate, phenoxyethyl acrylate, tetrahydrofurfuryl acrylate, glycidyl acrylate, dimethylaminoethyl acrylate, diethylaminoethyl acrylate, methyl methacrylate, ethyl methacrylate, butyl methacrylate, isobutyl methacrylate, cyclohexyl methacrylate, 2-ethylhexyl methacrylate, isodecyl methacrylate, lauryl methacrylate, stearyl
20 methacrylate, isobornyl methacrylate, benzyl methacrylate, hydroxyethyl methacrylate, hydroxypropyl methacrylate, methoxyethyl methacrylate, ethoxyethyl methacrylate, phenoxyethyl methacrylate, tetrahydrofurfuryl methacrylate, glycidyl methacrylate, dimethylaminoethyl methacrylate, diethylaminoethyl methacrylate, tert-butylaminoethyl methacrylate, acetoxylethyl methacrylate, acrylamide, N-methylolacrylamide, N-butoxyethylacrylamide, N,N-dimethylacrylamide, N-isopropylacrylamide, N-tert-butylacrylamide, N-tert-octylacrylamide, diacetone acrylamide, methacrylamide, N-methylolacrylamide, N,N-dimethylacrylamide, vinyl acetate, vinyl propionate, vinyl 2-ethylhexanoate, vinyl neodecanoate, vinyl stearate, N-vinylpyrrolidione, N-vinylcaprolactam, N-vinylformamide, N-vinylacetamide, methyl vinyl ether, ethyl vinyl
25 ether, butyl vinyl ether, decyl vinyl ether, hydroxybutyl vinyl ether, and combinations thereof.
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7. The method of claim 1 wherein the polymerization initiator comprises from about 0.5% to about 5.0% by total weight of the monomer mixture and is a member selected from the group consisting of thermal initiators, redox initiators, and combinations thereof.
- 5 8. The method of claim 1 wherein the unsaturated fatty acid is a member selected from the group consisting of fatty acids containing from 12 to 24 carbon atoms and at least one carbon-carbon double bond, and combinations thereof.
9. The method of claim 8 wherein the unsaturated fatty acid is a member selected from the group consisting of oleic acid, linoleic acid, linolenic acid, eleostearic acid, tall oil fatty acids, linseed oil fatty acids, tung oil fatty acids, safflower oil fatty acids, soybean oil fatty acids, and combinations thereof.
- 10 10. The method of claim 1 wherein the chain transfer agent is a member selected from the group consisting of dodecyl mercaptan, mercaptoacetic acid, mercaptopropionic acid, mercaptosuccinic acid, octyl mercaptan, 2-mercaptoethanol, and combinations thereof.
- 15 11. The method of claim 1 wherein the functional equivalents of dimer acid is a member selected from the group consisting of dicarboxylic acids containing two carboxyl groups and from 19 to 27 carbon atoms, and combinations thereof.
12. The method of claim 1 wherein the functional equivalents of trimer acid is a member selected from the group consisting of tricarboxylic acids containing three carboxyl groups and from 20 to 28 carbon atoms, and combinations thereof.
- 20 13. The method of claim 1 wherein the rosin is a member selected from the group consisting of tall oil rosin, wood rosin, gum rosin, and combinations thereof.
14. The carboxylic acid-modified vinylic polymeric composition of claim 1.
- 25 15. A latex comprising as a support resin an aqueous solution of the carboxylic acid-modified vinylic polymeric composition of claim 14.
16. An ink comprising the latex of claim 15.
17. The ink of claim 16 wherein the ink further comprises a pigment.
18. A varnish comprising the composition of claim 14.
- 30 19. A paint comprising the latex of claim 15.
20. The paint of claim 19 wherein the paint further comprises a pigment.

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	C08L51/00	C08F289/00			

B. FIELDS SEARCHED

IPC 7 C08F C09D C08L

WPI Data, PAJ, EPO-Internal

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 994 123 A (WESTVACO CORP) 19 April 2000 (2000-04-19) paragraph '0013!; claim 1 -----	1-19
A	US 5 216 064 A (RIVERA MARIA A ET AL) 1 June 1993 (1993-06-01) cited in the application claim 1 -----	1-19
A	US 4 839 413 A (KIEHLBAUCH RICHARD A ET AL) 13 June 1989 (1989-06-13) cited in the application claim 1 ----- -/--	1-19

☒ Patent family members are listed in annex.

*& document member of the same patent family

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Krail, G

INTERNATIONAL SEARCH REPORT

Intern ☐ Application No

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>DATABASE WPI Week 200040 Derwent Publications Ltd., London, GB; AN 2000-454647 XP002257033 & JP 2000 159867 A (HARIMA KASEI) abstract -----</p>	1-19

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

Internal Application No

PCT/US 03/20024

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0994123	A	19-04-2000	EP 0994123 A2	19-04-2000
			US 6433052 B1	13-08-2002
			US 6437033 B1	20-08-2002
			US 6172149 B1	09-01-2001
			US 6503971 B1	07-01-2003
			US 6329068 B1	11-12-2001
US 5216064	A	01-06-1993	EP 0566439 A2	20-10-1993
			JP 6206912 A	26-07-1994
US 4839413	A	13-06-1989	AT 74609 T	15-04-1992
			CA 1318426 C	25-05-1993
			DE 3778091 D1	14-05-1992
			EP 0257567 A2	02-03-1988
			ES 2030027 T3	16-10-1992
			JP 1924454 C	25-04-1995
			JP 6051733 B	06-07-1994
			JP 63083102 A	13-04-1988
			US 4820762 A	11-04-1989
			US 4954558 A	04-09-1990
JP 2000159867	A	13-06-2000	NONE	